Synthesis, hemilability, and catalytic transfer hydrogenation activity of iridium(III) and ruthenium(II) complexes containing oxygen-functionalised triazolylidene ligands

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Dedicated to Gerard van Koten on the occasion of his 75th birthday and in admiration of his pioneering and inspiring contributions to organometallic chemistry and catalysis

Abstract

The synthesis and characterisation of iridium(III) and ruthenium(II) complexes bearing pendant hydroxy- and ether-wingtip substituents is described. Both monodentate and *C*,*O*-bidentate binding modes were observed for these *O*-functionalised triazolylidene complexes. The two bonding modes are interconvertible, which demonstrates the hemilability of this coordinating group. The catalytic activity of the complexes was compared in transfer hydrogenation, revealing that pendant hydroxy-functionalities are beneficial for enhancing the performance of triazolylidene iridium(III) catalysts, while they have no effect in ruthenium-catalysed transfer hydrogenation. Accordingly, this functional group may serve as a probe to distinguish inner sphere from outer sphere transfer hydrogenation.

Highlights:

- New oxygen-functionalised ruthenium and iridium triazolylidene complexes
- Hydroxy group is hemilabile
- Hydroxy group accelerates hydrogen transfer catalysis mediated by iridium(III)

Introduction

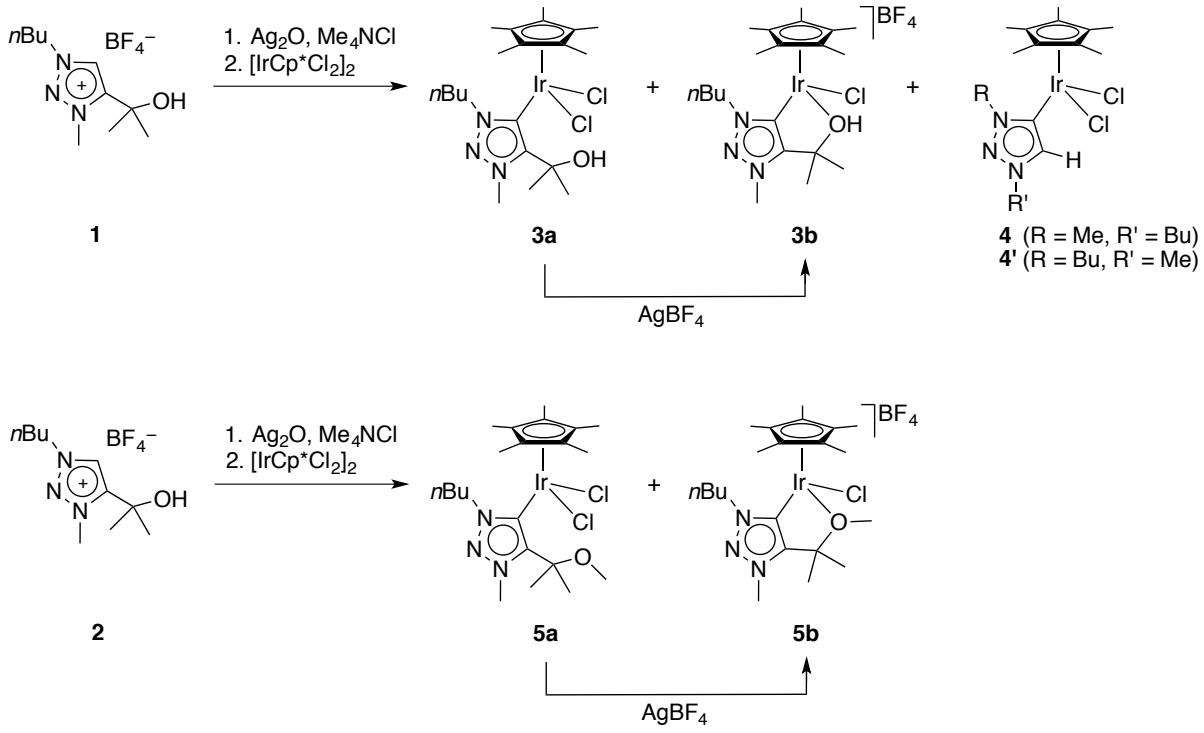
Pincer complexes have made one of the most fundamental contributions to the development of modern organometallic chemistry.[1] In pioneering work, van Koten and coworkers explored the consequences of combining hard amine donor sites with soft metals such as iridium(I) and platinum(II) nuclei,[2] which lead to a plethora of fascinating applications. Building on this fundamental design concept, we became interested in modifying N-heterocyclic carbenes (NHCs), a classic ligand scaffold of modern catalyst design as NHCs much like pincer ligands typically impart high thermal stability and countless options for synthetic modifications.[3] Introducing functional groups on the ligand scaffold allows for imparting stability through chelation, or hemilability for catalyst activation, or even bifunctional catalysis in which both the ligand and the metal participate in the conversion of substrate.[4] Prototypical examples of such functionalised catalysts include Shvo[5] and Noyori's[6] (de)hydrogenation catalysts, which have excellent activity in an extended range of applications.[7]

Based on these considerations, several examples of *O*- and *N*-functionalised Arduengo-type carbene complexes have been developed that display cooperative behaviour and enhanced catalytic properties.[8] Such functionalisation is even more versatile with 1,2,3-triazolylidene ligands,[9] as the core heterocycle is generally assembled via functional group-tolerant 'click' cycloaddition reaction of azides and alkynes.[10] Triazolylidene ligands that are *N1,N3*-disubstituted are mesoionic[11] and have been shown to stabilize high and low metal oxidation states.[12] They impart excellent catalytic activity in numerous transformations including cross-coupling,[13] and in particular redox transformations such as water oxidation,[14] amine and alcohol oxidation[15] and transfer hydrogenation.[16] While much recent work has been focusing on *C,N*-chelating triazolylidene complexes with imine donor sites, much less work has been directed towards understanding the catalytic implications of oxygen donors as functional groups at the triazolylidene ligand scaffold.[17] Due to the demonstrated benefits of oxygen functional groups in close proximity to the metal centre, we have designed triazolylidene metal complexes with a potential *C,O*-bidentate bonding motif.[8e,18] Herein we describe the synthesis of *O*-functionalised 1,2,3-triazolylidene iridium(III) and ruthenium(II) complexes and their catalytic activity in transfer hydrogenation. Specifically, we sought to introduce pendant oxygen-wingtip groups adjacent to the carbene, to investigate hemilabile coordination and potential metal-ligand cooperative behaviour in hydrogen transfer for (de)hydrogenation processes.

Results and Discussion

Synthesis and characterisation of 1,2,3-triazolylidene iridium(III) complexes. The hydroxy-functionalised ligand precursor **1** was prepared by literature procedures (Scheme 1).[18d] For the synthesis of the ether-functionalised triazolylidene precursor **2**, a Williamson ether synthesis using NaH

and MeI was applied at the triazole stage to install the methyl ether, followed by triazole *N*-alkyation with $[Me_3O]BF_4$, which afforded the triazolium salt **2** in high yields (74%). Conveniently, NaH was used as the commercially available oil dispersion without any negative impact on yield. The purity of the crude triazole intermediate was not an issue as any oil residues were readily washed off from the final triazolium product after subsequent *N*-alkylation. The iridium(III) complexes **3**–**5** were synthesised by transmetallation procedures from the corresponding triazolium salt **1** or **2**, using Ag_2O (2 equiv) and Me_4NCl (1 equiv) to form the Ag-carbene intermediates and subsequent *in situ* transmetallation with $[Ir(Cp^*)Cl_2]_2$ (0.38 equiv). This procedure yielded iridium complexes **3**–**4** when starting from the hydroxy-functionalised ligand precursor **1**, and complexes **5a,b** when starting from triazolium salt **2** with an ether wingtip group. All complexes were obtained in spectroscopically pure form after separation by column chromatography, except for regioisomers **4** and **4'**, which were not attempted to be separated any further. Satisfactory yields of *ca*. 40% were achieved for the desired *O*-functionalised iridium complexes, **3a** and **5a**. Complexes **3b** and **5b** were obtained in variable yields and purity from this transmetallation protocol. Oxygen chelation and formation of complexes **3b** and **5b** was more reliably achieved upon reaction of the monodentate triazolylidene complexes **3a** and **5a**, respectively, with $AgBF_4$ as chloride scavenger.



Scheme 1 Synthesis of 1,2,3-triazolylidene iridium(III) complexes **3**–**5**.

Regioisomers **4** and **4'** were obtained in addition to the *O*-functionalised complexes **3a,b**, as a consequence of wingtip degradation and formal loss of acetone, a reactivity pattern of this triazolium salt that was observed previously in the presence of Ag_2O in attempts to transmetallate to gold(I).[18d] These results support the hypothesis that degradation of this wingtip group is Ag-mediated. The regioisomers were isolated in a 1:1 mixture and were used without further separation for subsequent applications. Consequently, two sets of resonances were observed in both ^{1}H and ^{13}C NMR spectra and assignments were made using 2-dimensional spectroscopy, including nuclear Overhauser effect spectroscopy (NOESY). The appearance of two low-field C_{trz}–H resonances at δ_H = 7.49 and 7.51 in the ^{1}H NMR spectrum is diagnostic for the loss of the C–4 wingtip group and confirmed the formation of complexes **4** and **4'**. Also the carbenic chemical shifts for complexes **4** and **4'** (δ_C = 148.4 and 147.9) are well within the range reported for related triazolylidene iridium complexes. [14,15,19]

Triazolylidene bonding in a monodentate or *C*,*O*-bidentate mode in complexes **3a/5a** and **3b/5b**, respectively, was identified by the distinct ^{1}H NMR spectroscopic characteristics of these complexes. The NCH_2 hydrogens of the monodentate coordinated triazolylidene in complexes **3a** and **5a** are diastereotopic and separated by *ca*. 1 ppm (δ_H = 4.93 and 4.09 for **3a,** and multiplets centred at δ_H = 4.95 and 4.09 for **5a**). In contrast, this group appears in the chelating triazolylidene complex **3b** as a broad singlet at δ_H = 4.45, and in complex **5b** as two resonances with only 0.2 ppm shift difference (multiplets around δ_H = 4.5 and 4.3 ppm). In addition the ^{13}C NMR signals due to the triazolylidene carbons appear at 3–9 ppm higher field in the monodentate triazolylidenes (δ_C = 145.5 and 152.9 in **3a**, and 146.7 and 150.2 in **5a**) when compared to the chelating triazolylidene complexes (δ_C = 154.1 and 157.2 in **3b**, and 151.5 and 153.0 in **5b**). This shift correlates with the lower donor properties of the *O*-functionalities in comparison to the chloride ligand, resulting in a deshielding of the triazole carbons. Likewise, the ^{13}C resonances corresponding to the quaternary carbons of the *tert*–butyl group undergo a diagnostic shift upon chelation and appear at δ_C = 77.6 and 81.5 ppm, for **3b** and **5b**, respectively (*cf.* 69.0 and 76.5 ppm, for **3a** and **5a**, respectively), in agreement with a reduced electron density on the oxygen atom upon coordination to the metal centre.[20]

Chelation of the triazolylidene ligand in complexes **3b** and **5b** was further supported by chloride abstraction experiments performed with the monodentate triazolylidene complexes **3a** and **5a**. For example, reaction of these complexes with $AgBF_4$ (1 equivalent) in CH_2Cl_2 solution yielded complexes **3b** and **5b**, as corroborated by ^{1}H NMR spectroscopy. Similarly, when $NaBPh_4$ was used as the chloride scavenging agent, the highly diastereotopic NCH_2 hydrogens merged characteristically to a singlet for complexes **3b** and **5b**. While most NMR resonances are identical to those obtained from **3b**, the use of BPh_4^- counterion leads in addition to a 1:1 molar ratio between the metal complex and phenyl groups of the BPh_4^- anion (Supplementary Material, pages S10, S17), indicating that alternative chloride scavengers yield the same type of cationic chelate complexes.

Finally, the presence of the acidic OH protons in both **3a** and **3b** was confirmed by D_2O exchange experiments, which induced disappearance of the resonances at δ_H = 6.21 and 3.39 ppm for **3a** and **3b** respectively (CD_2Cl_2 solution). Interestingly, monocationic complexes analogous to **3b** could not be synthesised from closely related *O*-functionalised imidazolylidene iridium complexes (though MeCN was used as solvent *in lieu* of CH_2Cl_2).[8e]

Unambiguous evidence for the proposed structures was obtained from single crystal X-ray analyses of complexes **3a**,**b** and **5a** (Fig. 1, Table 1). The molecular structures show the typical piano-stool arrangement around iridium(III), and general metrics are unexceptional.[14,15,19] Analysis of the monodentate triazolylidene complexes **3a** and **5a** reveals only slight deviations of bond lengths and angles between these complexes. Complex **3b,** in contrast, displays *C*,*O*-bidendate coordination of the triazolylidene through both an Ir–$C_{carbene}$ and an Ir–O bond. The bond lengths vary only slightly upon chelation. The Ir–C and Ir–Cl bonds are contracted by *ca.* 0.04 Å in **3b** when compared to **3a** (*e.g.* Ir–C1 2.032(4) *vs* 2.077(3) Å), presumably as a consequence of the formally cationic nature of the metal centre in **3b**. Also, as a consequence of chelation, the Ir–C1–C2 angle in **3b** is smaller than the corresponding angle in **3a** (119.1(3) *vs* 136.7(2)°). This distortion is compensated by and inverse trend in the Ir–C1–N1 angle (increasing to 138.1(3)° in **3b** *vs.* 121.54(19)° in **3a**). Accordingly, the overall yaw angle is only marginally affected with 7.6° for **3a** and 9.0° for **3b.** Intramolecular H-bonding is observed in complex **3a** between the hydroxy functionality and the metal-bound chloride with a O–H…Cl donor-acceptor distance of 3.06 Å and a 166.2° hydrogen bond angle, thus forming a 7-membered metallacycle. Complex **3b** displays H-bonding between the coordinated alcohol and the non-coordinating BF_4^- anion with a O–H…F donor-acceptor distance of 2.63 Å and an angle of 174°. These H…X interactions fall within the range expected for moderate-strength H-bonds.[21] The Ir–O bond length in complex **3b** is 2.225(3) Å, slightly longer than the analogous bond distance in a related $[Ir(Cp^*)(trz\text{-}py)(OH_2)]^{2+}$ complex (*cf.* 2.166(3) Å),[19a] and at the upper end of related NHC iridium(III) complexes (Ir–O bond in 2.15–2.24 Å range).[8e,22] The relatively long Ir–O bond in **3b** has been attributed to the high steric bulk of the *tert*-butyl wingtip group.

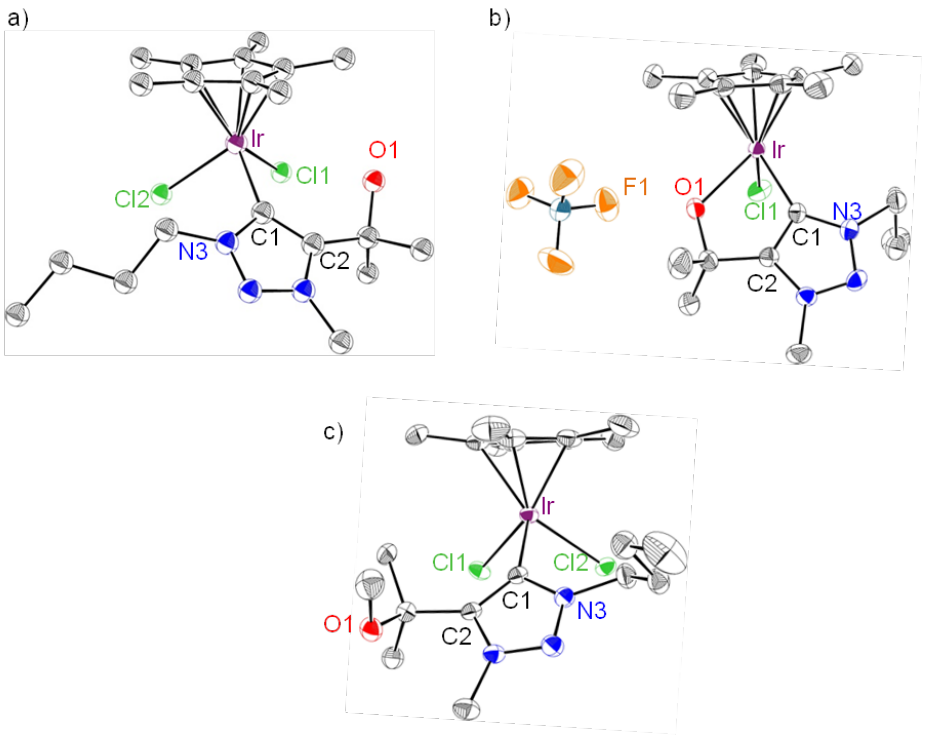


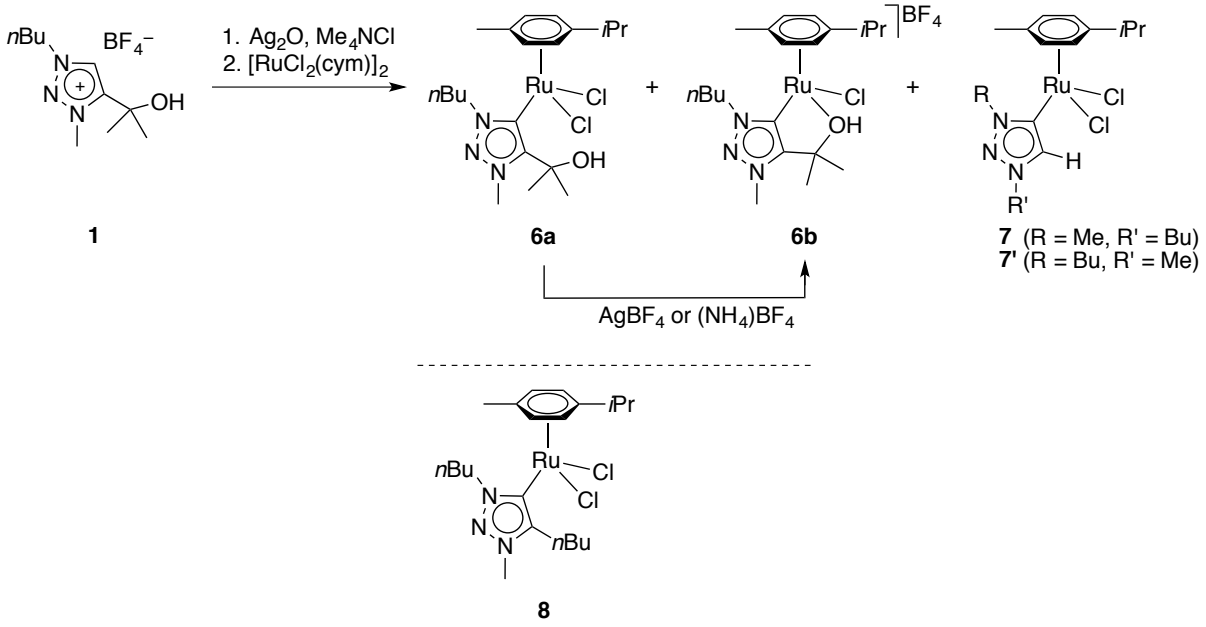
Figure 1: ORTEP representations of complex **3a** (a; only one of the two independent molecules shown), complex **3b** (b) and complex **5a** (c; all structures at 50% probability, disorder and hydrogen atoms omitted for clarity).

Table 1 Selected bond distances (Å) and angles (°) for complexes **3a**, **3b** and **5a**.

	3a (X = Cl2)[a)]	**3b** (X = O)	**5a** (X = Cl2)
Ir–C1	2.077(3)	2.032(4)	2.082(3)
Ir–Cl1	2.4237(7)	2.3779(10)	2.4184(8)
Ir–X	2.4271(7)	2.225(3)	2.4448(9)
C1–C2	1.403(4)	1.380(5)	1.405(5)
Ir-Centroid	1.807	1.785	1.814
C1–Ir–X	89.43(7)	73.61(12)	89.22(10)
C1–Ir–Cl1	92.13(8)	86.29(10)	89.67(10)
Cl1–Ir–X	86.33(3)	86.46(9)	84.02(10)
Ir–C1–C2	136.7(2)	119.1(3)	136.0(3)
Ir–C1–N3	121.54(19)	138.1(3)	121.9(2)

[a] Data only for one of the two (essentially identical) crystallographically independent molecules in the unit cell.

Synthesis and characterisation of *O*-functionalised 1,2,3-triazolylidene ruthenium(II) complexes. The synthetic methodology developed for *O*-functionalised triazolylidene iridium(III) complexes was successfully extrapolated to prepare analogous ruthenium(II) complexes. Thus, ruthenium complexes **6** and **7** were synthesised from ligand precursor **1** using ([Ru(*p*-cymene)Cl_2] (0.3 equivalents) instead of [Ir(Cp*)Cl_2]$_2$ for transmetallation (Scheme 2). Purification by column chromatography yielded complexes **6a**,**b** and **7**. Alternatively, complex **6a** was isolated selectively in up to 60% yield through an aqueous extraction of the crude reaction mixture followed by salting out the complex into CH_2Cl_2. This method of purification was applicable because in contrast to **6a**, complexes **7**/**7'** are insoluble in water. This difference in solubility is likely due to the presence of the hydoxy group in **6a** and is an additional benefit of incorporating the alcohol functionality, as a wide solubility range increases the scope for potential catalytic applications. The synthesis of ether-functionalised ruthenium complexes was probed using triazolium **2** in an analogous procedure. While ^{1}H NMR spectroscopy and specifically the diagnostic shifts of both the ligand and the *p*-cymene resonances suggest the formation of the product in the crude reaction mixture, the product was unstable and decomposed during purification, which prevented the isolation of a pure sample.



Scheme 2 Synthesis of 1,2,3-triazolylidene ruthenium(II) complexes **6** and **7**, and reference compound **8**.

In addition to complexes **6a,b**, the transmetallation procedure also yielded minor quantities of complexes **7** and **7'** as a result of the Ag-mediated degradation of the C4-wingtip group of triazolium salt **1**, analogously to complexes **4**. The nature of these complexes was confirmed by NMR spectroscopy and elemental analysis. Two sets of resonances were observed in the ^{1}H and ^{13}C spectra, confirming the presence of both regioisomers in a *ca*. 1:1 mixture. Purification by column chromatography provided pure complex **7** in small quantities, yet sufficient for unambiguous NMR characterisation of this complex. Consequently, this data in combination with NOESY experiments allowed also the ^{1}H and ^{13}C resonances of complex **7'** to be assigned from the mixed sample. The ^{1}H NMR spectrum of complexes **7** and **7'** features two resonances at δ_H = 7.63 and 7.59 ppm which are diagnostic for the loss of the C4-wingtip group. The triazolylidene ^{13}C NMR resonances of complex **7** were slightly deshielded when compared to the isomer **7'** (δ_C = 166.0 and 133.8 *vs.* 166.4 and 134.5). These data reflect the closely related structures of **7** and **7'** and the similar donor properties of the methyl and *n*-butyl groups.

The monodentate triazolylidene complex **6a** and the *C*,*O*-bidentate triazolylidene ruthenium complex **6b** were readily distinguished by their $C_{cym}H$ resonances in the 5.9–4.5 ppm range, and in particular by the resonance of the NCH_2 group, which appears as a triplet at δ_H = 4.56 in **6a**, while in **6b** this group gives rise to a multiplet at δ_H = 4.68–4.52. We note that the ^{1}H NMR spectrum of **6b** does not reveal diastereotopic resonances for the $C(CH_3)_2$ group of the *p*-cymene, even though the ruthenium(II) centre is stereogenic. The ^{13}C spectra revealed no distinct differences between **6a** and **6b,** and the carbenic resonances of these complexes are within the range reported for similar triazolylidene ruthenium complexes (δ_C = 164.8 and 163.9 for **6a** and **6b** respectively).[14a,15,16,23] NMR data was not sufficient to distinguish the structural motifs of **6a** and **6b,** and analogously to complexes **3** and **5** chloride scavenging reactions were used to identified the denticity of the triazolylidene ligand. Thus, addition of $AgBF_4$ (1 equivalent, CH_2Cl_2) or NH_4BF_4 (1 equivalent, acetone) to complex **6a** yielded **6b**, as evidenced by the diagnostic shift and splitting of the NCH_2 resonance in the ^{1}H NMR spectrum. When $NaBPh_4$ was used to abstract the chloride ligand from complex **6a**, the observed 1:1 ratio between the BPh_4^- anion and the ligand NMR resonances confirmed the monocationic nature of **6b**. Conversely, complex **6b** was converted to complex **6a** by the addition of brine to an aqueous solution of **6b** followed by extraction with CH_2Cl_2. This methodology is analogous to the aqueous purification of the reaction mixture (see above), which yielded exclusively complex **6a.** Accordingly, the presence of excess chloride ions induces metallacycle ring opening and the transformation of the chelate ligand in **6b** to a monodentate bonding mode in **6a**. The reversible interconversion of **6a** and **6b** demonstrates that the hydroxy group provides a hemilabile ligand site. Finally, D_2O exchange experiments confirmed the presence of acidic OH groups in both complexes **6a** and **6b** by the disappearance of the ^{1}H NMR resonances at δ_H = 9.46 and 9.34, respectively (D_6-DMSO solutions, Fig. S2–S4). These data confirm that the *C*,*O*-bidentate ligand in complex **6b** is formally neutral.

Transformation of **6b** to **6a** in aqueous media suggested that the chelating and the non-chelating triazolylidene binding mode may be interconvertible depending on the polarity of the solvent. NMR spectroscopic investigations of pure complexes **6a** and **6b** revealed no equilibrium in $CDCl_3$ and CD_2Cl_2 and each complex displayed its own characteristic resonance pattern for the cymene and NCH_2 group (*vida supra*). In CD_3OD, the aromatic cymene resonances of complex **6a** are relatively broad, while the resolution was unaltered for complex **6b**. The broadening observed in complex **6a** may hint towards an exchange in the ruthenium coordination sphere and competitive MeOH coordination (Fig. S4). In D_6–DMSO, **6a** and **6b** have identical ^{1}H NMR spectra (Fig. S2), indicating the formation of a cationic complex involving either *C*,*O*-bidentate triazolylidene chelation as in **6b**, or a Ru–DMSO bond formation by displacement of the chloride and the chelating-hydroxy ligands of **6a** and **6b**, respectively. Further characterization of this species was prevented by the gradual decomposition of both **6a** and **6b** in DMSO solution, evidenced by the appearance of ^{1}H resonances corresponding to free *p*-cymene already within the first few min. When dissolved in $CDCl_3$, CD_2Cl_2, or CD_3OD, complexes **6a**,**b** exhibited better stability and *p*-cymene loss was only observed after extended time periods (*ca*. 24 h, *i.e.* when cymene loss was complete in DMSO). For comparative purposes, D_6-DMSO solutions of the known[15a] ruthenium complex [Ru(1,4-dibutyl-triazolylidene)Cl_2(cymene)] as analogue of complexes **6a,b** displayed only *ca*. 2% free *p*-cymene even 2 days after sample preparation. Cymene loss is presumably promoted by the coordinating nature of the wingtip group, which is also corroborated by instability of related triazolylidene ruthenium(II) complexes containing an imine wingtip group.[15b]

Catalytic transfer hydrogenation. The pendant *O*-functionalities in complexes **3**,**5** and **6** provide opportunities for cooperative metal-ligand interaction and proton-shuttling, which is particularly beneficial in hydrogen transfer reactions.[4c,8,24] The catalytic activity of the novel iridium complexes **3**–**5** was therefore evaluated in transfer hydrogenation using standard reaction conditions, *i.e*. refluxing ^{i}PrOH as the sacrificial hydrogen source, KOH (10 mol% relative to the substrate) and benzophenone as model substrate.[25] An initial run with complex **3a** as catalyst precursor at 1 mol% loading produced the product alcohol in a moderate 67% yield after 8 h (Table 2, entry 1). Increasing the catalysts loading to 2 mol% enhanced the performance and gave quantitative conversions when using the *O*-functionalised iridium complexes **3a** and **3b** (entries 2,3). A time conversion profile indicated no significant difference in performance of these two complexes (Fig. 2), suggesting that the catalytically active species formed from **3a** and **3b** is identical. In comparison, complex **4** containing an unfunctionalised triazolylidene ligand only achieved 39% conversion within the same reaction time. This substantial reactivity difference emphasizes the beneficial role of the hydroxy functionality. Moreover, it indicates that the functional wingtip group is resistant to base-mediated degradation as observed in the presence of Ag_2O (*cf.* formation of **4** during the metalation process). The presence of

an ether functionality as triazolylidene wingtip group as in complex **5a** improves the activity of the iridium centre slightly when compared to the unfunctionalised ligand in **4** (65%, entry 4), though the performanc is still significantly lower than in the presence of a hydroxy group. These data suggest that the hydroxy group plays a distinct role, likely in the formation of a metal-bound alkoxide as an anionic *C,O*-bidentate chelate.[26] Such alkoxide formation increases the electron density at the iridium centre and therefore enhance its catalytic activity in transfer hydrogenation. Alternatively, the alkoxy group may facilitate formal dihydrogen abstraction from *i*PrOH via an outer sphere mechanism, involving transfer of the hydride to the iridium centre and proton transfer to the ligand oxygen.[8d,e] In stoichiometric experiments, reaction of **3b** with Cs_2CO_3 as a base indeed revealed formation of a new species with a ^1H resonance pattern distinct from **3a** and **3b** (e.g. NCH_2 appears as a multiplet at 4.27–4.18 ppm), which has been assigned tentatively to the deprotonated alkoxide species.

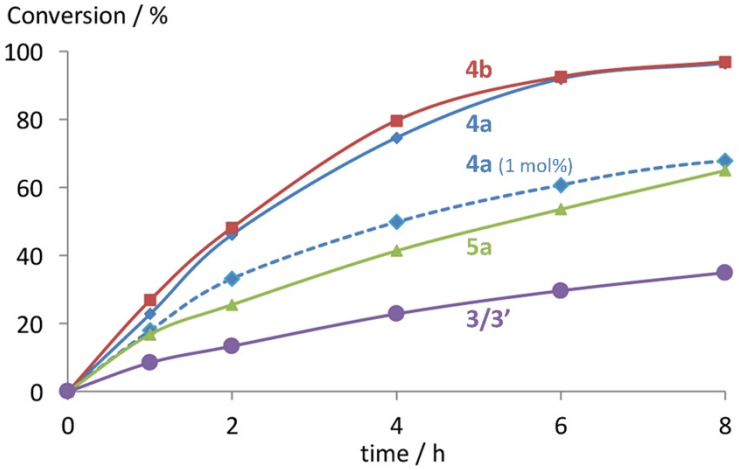
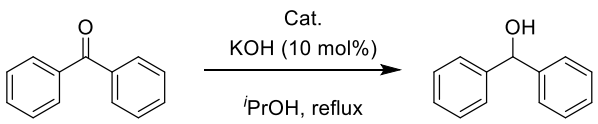


Figure 2 Time-dependent profile for the catalytic transfer hydrogenation of benzophenone with complexes **3–5** (solid lines: S/C/B ratio 50:1:5, 2 mol% complex; dashed lines: S/C/B ratio 100:1:10, 1 mol% complex).

Table 2 Catalytic transfer hydrogenation of benzophenone.[a]



entry	cat.	mol%	time (h) / conv (%)[b]	Time (h) / conv. (%)[b]	TOF_{50} (h^{-1})[c]
1	**3a**	1	2 / 33	8 / 67	12

2	**3a**	2	2 / 46	8 / 96	12
3	**3b**	2	2 / 48	8 / 97	12
4	**4/4'**	2	2 / 13	8 / 35	2
5	**5a**	2	2 / 26	8 / 65	4
6	**6a**	1	0.5 / 78	1.5 / 97	210
7	**6b**	1	0.5 / 76	1.5 / 98	200
8	**8**	1	0.5 / 95	1.5 / 98	370

[a] General reaction conditions: Benzophenone (0.5 mmol or 1.0 mmol), KOH (10 mol%), [Ir] (0.01 mmol), 2-propanol (5 mL), reflux temperature; [b] Conversions determined by ^{1}H NMR spectroscopy using mesitylene as internal standard, averaged over 2 runs; [c] TOF_{50} determined at 50% conversion.

The ruthenium complexes **6a**,**b** were considerably more active than their iridium analogues in transfer hydrogenation under otherwise identical conditions and reached full conversion within 1 h when used at 1 mol% loading (Table 2, entries 6,7). Again, both complexes showed a reactivity profile that is identical within standard errors (Fig. S1). The analogous ruthenium complex **8** containing a 1,4-dibutyl-triazolylidene ligand[15a] was evaluated for comparison and reached 92% conversion within 15 min (*cf.* 51% for complexes **6a** and **6b**) and essentially complete conversion after 30 min (entry 8). The higher activity of complex **8** (TOF = 370 h^{-1} *vs* about 200 h^{-1} for complexes **6a,b**) indicates no beneficial role of the hydroxy group in the ruthenium system. These data are in agreement with an inner sphere monohydride mechanism,[27] in which the critical hydride species is formed via β-hydrogen elimination of metal-coordinated isopropoxide without any participation of ancillary ligands.

Previous studies revealed that triazolylidene ruthenium(II) complexes are more active transfer hydrogenation catalysts than their iridium(III) analogues.[16b,c] Likewise, ruthenium complex **6a** reaches nearly quantitative conversion within 1 h, and is more than an order of magnitude more active than its iridium analogue **3a** which reaches only 18% conversion in the same time (TOF 210 h^{-1} vs 12 h^{-1}). The different role of the hydroxy wingtip group in the iridium and ruthenium complexes suggests a different pathway for dihydrogen transfer from the *i*PrOH donor to the catalyst, and due to the microscopic reversibility, also from the catalyst to the substrate ketone. However, the hydrogen substituent of the triazolylidene in complex **4** may be susceptible to deprotonation thereby deactivating the catalyst. Therefore, it is clear that the catalytic activity of complexes **7**/**7'** or the iridium analogue of complex **8** is needed to make an unambiguous comparison between working modes of the iridium and ruthenium complexes with *O*-functionalised triazolylidene ligands, and will be included in future work. Finally, in comparison to other 1,2,3-triazolydene complexes employed in transfer hydrogenation, the iridium complexes reported here perform only moderately, while the ruthenium complexes are comparable to other carbene-based systems.[16]

Conclusions

O-functionalised 1,2,3-triazolyldiene iridium(III) and ruthenium(II) complexes were synthesised and applied in transfer hydrogenation. Ether- and hydroxy-substituted 1,2,3-triazolylidene iridium(III) complexes were isolated with the ligand both in mono- and bidentate coordination mode. Also, monodentate and *C*,*O*-bendate, hydroxy-functionalised 1,2,3-triazolylidene ruthenium complexes are described. The monodentate complexes were converted to the chelating species by chloride abstraction and *vice versa*, the chelates were transformed into monodentate ligands in the presence of excess halide. Transfer hydrogenation studies revealed that pendant hydroxy-donors substantially enhance the catalytic activity of the triazolylidene iridium(III) catalyst while analogous hydroxy-functionalised triazolylidene ruthenium(II) complexes did not outperform analogous unfunctionalised complexes. Generally, activity was much higher for the ruthenium(II) complexes than the iridium(III) homologues, which hints towards diverging activation mechanisms. Caution is therefore required when generalising beneficial ligand features. Future outlooks include a detailed investigation into the activity of the ruthenium complexes in transfer hydrogenation to conclusively determine the influence of the hydroxy-group. Also, applications in base free oxidations and N-alkylation reactions pose exciting avenues of research to determine the influence of *O*-functionality in other (de)hydrogenation processes.

Experimental Section

General Procedures. Ag_2O was used after regeneration by heating >160 °C under vacuum. $[Ir(Cp^*)Cl_2]_2$,[28] 1-butyl-4-(CMe_2OH)-triazole,[18d] **1**,[18d] and **8** [15a] were prepared according to reported procedures. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on Bruker and Varian spectrometers operating at room temperature. Chemical shifts (δ in ppm, coupling constants *J* in Hz) were referenced to residual solvent resonances and are given downfield from $SiMe_4$. Elemental analysis and mass spectrometry were carried out by the microanalytical services of University College Dublin and University of Bern.

Triazolium salt 2. Under a N_2 atmosphere, 1-butyl-4-(CMe_2OH)-triazole (0.914 g, 5.0 mmol) was dissolved in dry THF (20 mL) and cooled to 0 °C. To this solution, NaH (60% in mineral oil, 0.30 g, 7.5 mmol) was added in 3 portions. The temperature was maintained at 0 °C for 15 min, after which the reaction mixture was allowed to stir at room temperature for 1 h. Iodomethane (0.50 mL, 8.0 mmol) was added to the reaction mixture, which was stirred for a further 1 h. Then H_2O (100 mL) was slowly added and the mixture was stirred for 30 min. The reaction mixture was extracted with Et_2O (3 x 100 mL). The organic fractions were combined and washed with brine (2 x 100 mL), dried with Na_2SO_4,

filtered and all volatiles removed under reduced pressure, yielding 1-butyl-4-(CMe_2OMe)-triazole as a pale yellow oil. This intermediate was purified by column chromatography (SiO_2; EtOAc/pentane, 2:1), however the crude form was suitable to be used for the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1H, $C_{trz}H$), 4.34 (t, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 3.14 (s, 3H, OCH_3), 1.95–1.83 (m, 2H, NCH_2CH_2), 1.61 (s, 6H, $C(CH_3)_2$), 1.43–1.30 (m, 2H, CH_2CH_3), 0.96 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_2CH_3) $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 152.7 ($C_{trz}C$), 120.4 ($C_{trz}H$), 73.1 ($C(CH_3)_2$), 50.7 (OCH_3), 50.1 (NCH_2), 32.4 (NCH_2CH_2), 26.7 ($C(CH_3)_2$) 19.9 (CH_2CH_3), 13.6 (CH_2CH_3). The 1-butyl-4-(CMe_2OMe)-triazole was dissolved in dry CH_2Cl_2 (30 mL). Then Me_3OBF_4 (0.845 g, 5.0 mmol) was added and the suspension stirred for 20 h under a N_2 atmosphere. MeOH (5 mL) was added and stirring continued for 30 min. All volatiles were removed under reduced pressure and the residual brown oil was dissolved in a minimal amount of CH_2Cl_2 and precipitated by addition of pentane (200 mL). The residue was collected by decantation and dried under reduced pressure. The solid was then dissolved in CH_2Cl_2 (50 mL) and stirred with activated carbon (100–325 mesh, 6 g) for 10 min. The suspension was filtered over Celite, and volatiles removed under reduced pressure. The residue was redissolved in a minimum amount of CH_2Cl_2 and added dropwise to cold Et_2O with vigorous stirring. The white precipitate was collected by decantation and thoroughly dried to yield the title product as a white solid (1.11 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H, $C_{trz}H$), 4.60 (t, $^3J_{HH}$ = 7.5 Hz, 2H, NCH_2), 4.36 (s, 3H, NCH_3), 3.20 (s, 3H, OCH_3), 2.07–19.5 (m, 2H, NCH_2CH_2), 1.70 (s, 6H, $C(CH_3)_2$), 1.48–1.36 (m, 2H, CH_2CH_3), 0.98 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 146.9 ($C_{trz}C$), 130.0 ($C_{trz}H$), 72.8 ($C(CH_3)_2$), 54.2 (NCH_2), 51.4 (OCH_3), 39.7 (NCH_3), 31.1 (NCH_2CH_2), 25.5 ($C(CH_3)_2$), 19.6 (CH_2CH_3), 13.4 (CH_2CH_3) HRMS (ESI +): *m/z* Found 212.1757 $[M–BF_4]^+$ (calcd for $C_{11}H_{22}N_3O$, 212.1763) Anal. Calc. for $C_{11}H_{22}BF_4N_3O$: C, 44.17; H, 7.41; N, 14.05%. Found: C, 43.74, H, 7.27; N, 13.96%.

Complexes 3 and 4. A suspension of **1** (170 mg, 0.60 mmol), Me_4NCl (66 mg, 0.60 mmol), Ag_2O (280 mg, 1.2 mmol) in CH_2Cl_2/MeCN (1:1 v/v, 10 mL) was stirred protected from light for 16 h. The suspension was filtered through Celite, eluted with CH_2Cl_2 (100 mL), and $[Ir(Cp^*)Cl_2]_2$ (180 mg, 0.23 mmol) added and the reaction mixtures stirred for 5 h protected from light. The reaction mixture was filtered over Celite, eluting with CH_2Cl_2 and the volatiles were removed under reduced pressure to yield the crude reaction mixture. Purification by column chromatography (SiO_2; CH_2Cl_2/MeOH gradient, 20:1 to 5:1) yielded complex **3a** (yellow solid, 120 mg, 43%), **3b** (yellow-brown solid, 58 mg, 20%) and complexes **4** and **4'**(1:1 mixture, hydroscopic yellow solid, 43 mg, 17%).

*Analytical data of complex **3a**.* ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.21 (br, 1H, OH), 4.93 (br, 1H, NCH_2), 4.09 (s, 4H, NCH_3 and NCH_2), 2.04 (br s, 2H, NCH_2CH_2), 1.64 (s, 6H, $C(CH_3)_2$), 1.56 (s, 15H, $C_{Cp}CH_3$), 1.50–1.44 (m, 2H, CH_2CH_3), 1.00 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2): δ 152.9 (C_{trz}), 145.5 (C_{trz}), 88.7 (C_{Cp}), 69.0 ($C(CH_3)_2$), 55.2 (NCH_2), 39.7 (NCH_3), 33.4 (NCH_2CH_2), 30.5 (br, $C(CH_3)_2$), 20.7 (CH_2CH_3), 14.2 (CH_2CH_3), 9.5 ($C_{Cp}CH_3$). HRMS (ESI^+): m/z

Found 560.2002 $[M–Cl]^+$ (cald for $C_{20}H_{34}ON_3ClIr$, 560.2014). Anal. Calcd for $C_{20}H_{34}N_3Cl_2IrO$: C, 40.33; H, 5.75; N, 7.05%; Found: C, 40.04; H, 5.64; N, 6.95%.

Analytical data of complex ***3b***. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.45 (br, 2H, NCH_2), 4.10 (s, 3H, NCH_3), 3.39 (br, 1H, OH), 2.05–1.93 (m, 2H, NCH_2CH_2), 1.73 (s, 15H, $C_{Cp}CH_3$), 1.65 (s, 6H, $(C(CH_3)_2)$, 1.47–1.33 (m, 2H, CH_2CH_3), 0.98 (t, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): 157.2 ($C_{trz}C$), 154.1 (C–Ir), 89.4 (C_{Cp}), 77.6 ($C(CH_3)_2$), 54.1 (NCH_2), 37.7 (NCH_3), 32.4 (NCH_2CH_2), 28.7 ($C(CH_3)_2$), 20.3 (CH_2CH_3), 13.9 (CH_2CH_3), 10.2 ($C_{Cp}CH_3$). HRMS (ESI^+): *m/z* Found 524.2240 $[M–H–Cl–BF_4]^+$ (cald for $C_{20}H_{33}ON_3Ir$, 524.2247). Despite numerous attempts and spectral purity of the compound (see Supplementary Material), no satisfactory microanalysis data could be obtained. Closest values are: Anal. Calcd for $C_{20}H_{34}BClF_4IrN_3O$: C, 37.13; H, 5.30; N, 6.49%; Found: C, 38.14; H, 5.48; N, 6.54%.

Analytical data of complex ***4***. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.49 (s, 1H, $C_{trz}H$), 4.50–4.46 (m, 2H, NCH_2), 4.05 (s, 3H, NCH_3), 2.09–1.98 (m, 2H, NCH_2CH_2), 1.59 or 1.58 (s, 15H, $CpCH_3$), 1.53–1.42 (m, 2H, CH_2CH_3), 0.99 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 148.4 (C_{trz}–Ir), 134.8 ($C_{trz}C$), 88.3 (C_{Cp}), 53.7 (NCH_2), 38.8 (NCH_3), 31.9 (NCH_2CH_2), 20.2 (CH_2CH_3), 13.7 (CH_2CH_3), 9.13 or 9.12 ($C_{Cp}CH_3$).

Analytical data of complex ***4'***. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.51 (s, 1H, $C_{trz}H$), 4.29 (t, 2H, $^3J_{HH}$ = 7.3 Hz, NCH_2), 4.25 (s, 3H, NCH_3), 2.09–1.98 (m, 2H, NCH_2CH_2), 1.59 or 1.58 (2 x s, 15H, $CpCH_3$), 1.42–1.30 (m, 2H, CH_2CH_3), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 147.9 (C_{trz}–Ir), 134.1 ($C_{trz}C$), 88.3 (C_{Cp}), 52.4 (NCH_2), 40.3 (NCH_3), 33.2 (NCH_2CH_2), 20.7 (CH_2CH_3), 14.2 (CH_2CH_3), 9.13 or 9.12 ($C_{Cp}CH_3$) HRMS (ESI^+): *m/z* Found 502.1580 $[M–Cl]^+$ (cald for $C_{17}H_{28}N_3ClIr$, 502.1596).

Complexes 5. A suspension of **2** (150 mg, 0.50 mmol), Me_4NCl (55 mg, 0.50 mmol), Ag_2O (233 mg, 1.0 mmol) in MeCN (10 mL) was stirred protected from light for 24 h. The suspension was then filtered through Celite, and the volatiles removed under reduced pressure. The residue was suspended in CH_2Cl_2 (20 mL) and $[Ir(Cp^*)Cl_2]_2$ (150 mg, 0.19 mmol) was added. The reaction mixture was stirred for 5 h protected from light, then filtered over Celite, and all volatiles were removed under reduced pressure to yield the crude products. Purification by column chromatography (SiO_2; CH_2Cl_2/MeOH gradient, 20:1 to 10:1) yielded product **5a** (100 mg, 42%) and **5b** (62 mg, 23%) as orange solids.

Analytical data of complex ***5a***. ^{1}H NMR (400 MHz, CD_2Cl_2): 5.01–4.84 (m, 1H, NCH_2), 4.19 (s, 3H, NCH_3), 4.15–4.01 (m, 1H, NCH_2), 3.06 (s, 3H, OCH_3), 2.13–1.96 (m, 2H, NCH_2CH_2), 2.04 (s, 3H, $C(CH_3)_2$), 1.76 (s, 3H, $C(CH_3)_2$), 1.66–1.39 (m, 2H, CH_2CH_3), 1.53 (s, 15 H, $C_{Cp}CH_3$) 1.01 (t, 3H,

CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): 150.2 ($C_{trz}C$), 144.7 (C_{trz}–Ir), 88.4 (C_{Cp}), 76.5 ($C(CH_3)_2$), 56.1 (NCH_2), 50.0 (OCH_3), 41.0 (NCH_3), 33.6 (NCH_2CH_2), 28.6, 25.3 ($C(CH_3)_2$), 20.8 (CH_2CH_3), 14.3 (CH_2CH_3), 9.70 ($C_{Cp}CH_3$). HRMS (ESI^+): *m/z* Found 574.2161 $[M–Cl]^+$ (cald for $C_{21}H_{36}ON_3ClIr$, 574.2171) Anal. Calcd for $C_{21}H_{26}N_3Cl_2IrO$: C, 41.37; H, 5.95; N, 6.89%; Found: C, 41.43; H, 5.95; N, 6.74%.

Analytical data of complex ***5b***. ^1H NMR (400 MHz, CD_2Cl_2): δ 4.57–4.49, 4.37–4.27 (2 x m, 1H, NCH_2), 4.13 (s, 3H, NCH_3), 3.70 (s, 3H, OCH_3), 2.02–1.85 (m, 2H, NCH_2CH_2), 1.67 (s, 15H, $C_{Cp}CH_3$), 1.61, 1.60 (2 x s, 3H, $C(CH_3)_2$), 1.41–1.30 (m, 2H, CH_2CH_3), 0.95 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): 153.0 (C_{trz}–Ir), 151.5 ($C_{trz}C$), 89.9 (C_{Cp}), 81.5 ($C(CH_3)_2$), 54.8 (OCH_3), 54.3 (NCH_2), 38.3 (NCH_3), 32.3 (NCH_2CH_2), 25.2, 24.6 (2 x $C(CH_3)_2$), 20.2 (CH_2CH_3), 13.9 (CH_2CH_3), 10.2 ($C_{Cp}CH_3$). HRMS (ESI^+): *m/z* Found 574.2158 $[M–BF_4]^+$ (cald for $C_{21}H_{36}ON_3ClIr$, 574.2171). Elemental analyses consistently showed high C values (by 1-2% and low H values (1%), even though the compounds were NMR spectroscopically pure.

Complexes 6 and 7. A suspension of **1** (170 mg, 0.60 mmol), Me_4NCl (66 mg, 0.60 mmol), Ag_2O (280 mg, 1.2 mmol) in CH_2Cl_2/MeCN (1:1 v/v, 10 mL) was stirred protected from light for 16 h. The suspension was filtered through Celite, eluted with CH_2Cl_2 (100 mL), and [Ru(*p*-cymene)Cl_2]$_2$ (110 mg, 0.18 mmol) added. The reaction mixture was stirred for 2 h protected from light, filtered over Celite, evaporated to dryness under reduced pressure. The crude reaction mixture was purified by column chromatography (SiO_2; CH_2Cl_2/MeOH gradient, 20:1 to 5:1), which yielded complex **6a** (50 mg, 28%) and complex **6b** (57 mg, 28%) both as a red-brown, hygroscopic solids, and complexes **7** and **7'** in a 1:1 mixture as a brown, hygroscopic solid (22.5 mg, 14%).

Alternately complex **6a** was isolated selectively by applying an alternative purification procedure. The crude reaction mixture was suspended in CH_2Cl_2 (100 mL) and extracted with H_2O (100 mL). CH_2Cl_2 (100 mL) was added to the aqueous phase followed by brine (200 mL) and the mixture extracted. The organic phase was dried over Na_2SO_4, filtered and the volatiles were removed under reduced pressure. Residual [Ru(*p*-cymene)Cl_2]$_2$ was removed from this residue by washing a CH_2Cl_2 (100 mL) solution of the product with several amounts of saturated NH_4Cl_{aq} until the aqueous phase was colourless. The crude product was purified by column chromatography (SiO_2; CH_2Cl_2/MeOH, 10:1-5:1 gradient), yielding **6a** as a red-brown, hygroscopic solid (104 mg, 57%)

Analytical data of complex ***6a***. ^1H NMR (400 MHz, CD_2Cl_2): 5.82, 5.73, 5.68, 5.18 (4 x br. s, 1H, H_{cym}), 4.56 (t,$^3J_{HH}$ = 7.4 Hz, NCH_2), 3.97 (s, 3H, NCH_3), 2.81–2.66 (m, 1H, $CHMe_2$), 2.14 (s, 3H, $C_{cym}CH_3$), 2.11–1.99 (m, 2H, NCH_2CH_2), 1.62, 1.54 (2 x br. s, 3H, $C(CH_3)_2$), 1.52–1.38 (m, 2H, CH_2CH_3), 1.17 (d,$^3J_{HH}$ = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.01 (t, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 164.8 (C_{trz}–Ru), 152.3 ($C_{trz}C$), 104.5 ($C_{cym}CH$), 100.7 ($C_{cym}CH_3$), 86.5 , 82.0, 79.0 (4 x $C_{cym}H$), 76.1 ($C(CH_3)_2$), 54.3 (NCH_2), 37.1 (NCH_3), 32.3 (NCH_2CH_2), 31.5 ($CHMe_2$), 29.3, 28.9 (2

x C(CH_3)$_2$), 23.3, 22.3 (2 x CH(CH_3)$_2$), 20.5 (CH_2CH_3), 19.3 ($C_{cym}CH_3$), 13.9 (CH_2CH_3). HRMS (ESI$^+$): *m/z* Found 468.1342 [M–Cl]$^+$ (calcd. for $C_{20}H_{33}ON_3ClRu$, 468.1350) Anal. Calcd for $C_{20}H_{33}N_3Cl_2ORu$: C, 46.35; H, 6.44; N, 8.01%; Found: C, 46.48; H, 6.50; N, 7.88%.

Analytical data of complex ***6b****.* ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.85–5.79 (m, 2H, H_{cym}), 5.49 (d, $^3J_{HH}$ = 6.0 Hz, 1H, H_{cym}), 5.18 (d, $^3J_{HH}$ = 5.9 Hz, 1H, H_{cym}), 4.68–4.52(m, 2H, NCH_2), 4.01 (s, 3H, NCH_3), 2.79–2.64 (m, 1H, $CHMe_2$), 2.16 (s, 3H, $C_{cym}CH_3$), 2.09–1.96 (m, 2H, NCH_2CH_2), 1.58 (s, 6H, C(CH_3)$_2$), 1.51–1.36 (m, 2H, CH_2CH_3), 1.21 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.01 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 163.9 (C_{trz}–Ru), 149.0 (C_{trz}C), 106.4 ($C_{cym}CH_3$), 100.8 (C_{cym}CH), 86.3, 82.0, 80.5, 79.0 (4 x C_{cym}H), 77.5 (C(CH_3)$_2$), 54.6 (NCH_2), 37.5 (NCH_3), 32.2 (NCH_2CH_2), 31.7 ($CHMe_2$), 28.5, 28.3 (2 x C(CH_3)$_2$), 23.1, 22.2 (2 x CH(CH_3)$_2$), 20.5 (CH_2CH_3), 19.3 ($C_{cym}CH_3$), 13.9 (CH_2CH_3). HRMS (ESI$^+$): *m/z* Found 468.1342 [M–BF_4]$^+$ (calcd. for $C_{20}H_{33}ON_3ClRu$, 468.1350). Like for the other *C,O*-bidentate triazolylidene complexes, no satisfactory microanalysis could be obtained for this complex.

Analytical data of complex 7. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.63 (s, 1H, C_{trz}H), 5.28 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 5.14 (d, $^3J_{HH}$ = 5.8 Hz, 2H, H_{cym}), 4.32–4.24 (m, 5H,NCH_3 and NCH_2), 2.65 (hept, $^3J_{HH}$ = 6.9 Hz,1H, $CHMe_2$), 2.09 (s, 3H, $C_{cym}CH_3$), 1.96–1.86 (m, 2H, NCH_2CH_2), 1.45–1.31 (m, 2H, CH_2CH_3), 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH(CH_3)$_2$), 0.97 (t, 3H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 166.0 (C_{trz}–Ru), 133.8 (C_{trz}H), 104.1 (C_{cym}CH), 100.7 ($C_{cym}CH_3$), 84.8, 84.3 (2 x C_{cym}H), 52.3 (NCH_2), 41.0 (NCH_3), 31.9 (NCH_2CH_2), 31.3 ($CHMe_2$), 22.6 (CH(CH_3)), 20.2 (CH_2CH_3), 18.7 ($C_{cym}CH_3$), 13.7 (CH_2CH_3).

Analytical data of complex ***7'.*** ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.59 (s, 1H, C_{trz}H), 5.27 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_{cym}), 5.12 (d, $^3J_{HH}$ = 6.1 Hz, 2H, H_{cym}), 4.58–4.49 (m, 2H, NCH_2), 4.04 (s, 3H, NCH_3), 2.76–2.66 (m, 1H, $CHMe_2$), 2.08 (s, 3H, $C_{cym}CH_3$), 2.07–1.96 (m, 2H, NCH_2CH_2), 1.55–1.44 (m, 2H, CH_2CH_3), 1.20 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH(CH_3)$_2$), 1.01 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_2CH_3). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 166.4 (C_{trz}–Ru), 134.5 (C_{trz}H), 104.3 (C_{cym}CH), 99.6 ($C_{cym}CH_3$), 84.9, 84.5 (2 x C_{cym}H), 52.3 (NCH_2), 38.8 (NCH_3), 33.8 (NCH_2CH_2), 31.2 ($CHMe_2$), 22.6 (CH(CH_3)$_2$), 20.7 (CH_2CH_3), 18.7 ($C_{cym}CH_3$), 14.2 (CH_2CH_3). HRMS (ESI$^+$): *m/z* Found 410.0929 [M–Cl]$^+$ (cald for $C_{17}H_{27}N_3ClRu$, 410.0932) Anal. Calcd for $C_{17}H_{27}N_3Cl_2Ru$: C, 45.84; H, 6.11; N, 9.43%; Found: C, 45.85; H, 6.09; N, 9.03%.

Chelation of monodentate ligands. *$AgBF_4$ as chloride scavenging agent.* To a solution of the corresponding metal complex (1 eq.) in CH_2Cl_2 (2 mL) was added $AgBF_4$ (1 eq.) followed by CH_2Cl_2 (3 mL). The reaction mixture was stirred for 15 min while protected from light, filtered over Celite and the volatiles were removed under reduced pressure. Further purification included gradient column

chromatography (SiO_2; CH_2Cl_2 to MeOH). Alternatively, a solution of the metal complex (1 eq.) in acetone (2 mL) was treated with $(NH_4)BF_4$ or $NaBPh_4$ (1 eq.) in acetone (3 mL). The reaction mixture was stirred for 18 h, all volatiles were removed under reduced pressure, and the residue was suspended in CH_2Cl_2 and filtered over Celite.

General procedure for catalytic transfer hydrogenation. In a one-necked round bottom flask metal complex (1.0 mmol), 2-propanol (5 mL) and mesitylene (0.36 mmol or 0.72 mmol) were mixed and aqueous KOH (2.0 M, 0.05 mmol or 0.1 mmol, 10 mol% relative to substrate) added and the mixture heated to a vigorous reflux for 10 minutes. Benzophenone (0.5 mmol or 1.0 mmol) was added, and aliquots (0.1 mL) were taken and directly dissolved in $CDCl_3$ (0.7 mL) and analysed by ^1H NMR spectroscopy, using mesitylene as internal standard.

Crystal Structure Determination. Crystal data of **3a**, **3b**, and **5a** were collected on a *Oxford Diffraction SuperNova* area-detector diffractometer using mirror optics monochromated Mo *K*α radiation (λ = 0.71073 Å) and Al filtered. Data reduction was performed using the *CrysAlisPro* program.[29] The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method using SCALE3 ABSPACK in *CrysAlisPro*[29] was applied. The structure was solved by direct methods using *SHELXT*,[30] which revealed the positions of all non-hydrogen atoms of the title compound. The non-hydrogen atoms were refined anisotropically. All H-atoms were placed in geometrically calculated positions and refined using a riding model. Refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. All calculations were performed using the *SHELXL-2014/7* program.[31] Further crystallographic details are compiled in Table S1–S3. Crystallographic data for the structures of all compounds reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers numbers 1537332 (**3a**), 1537334 (**3b**), and 1537333 (**5a**).

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Supplementary Material

Crystallographic details, NMR spectra, and time-conversion profiles for catalytic transfer hydrogenation with ruthenium complexes.

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